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FINAL REPORT

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INTERCHANGE FOR JOINT RESEARCH ENTITLED:

MEASUREMENT OF STABLE NITROGEN AND SULFUR ISOTOPES

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Viking measurements of the Martian atmosphere indicate a value of $^{15}N/^{14}N$ which is markedly greater than that found in Earth's atmosphere. These isotopic measurements provide a powerful diagnostic tool which may be used to derive valuable information regarding the past history of Mars and they have been used to place important constraints on the evolution of Mars' atmosphere. Initial partial pressures of nitrogen, outgassing rates, and integrated deposition of nitrogen into minerals have been calculated from this important atmospheric data (McElroy *et al.*, 1976 and 1977; Fox and Dalgarno, 1983). The greater precision obtained in laser spectrometer isotopic measurements compared to the Viking data will greatly improve these calculated values.

It has also been proposed that the $^{15}N/^{14}N$ value in Mars' atmosphere has increased monotonically over time (McElroy *et al.*, 1977; Fox and Dalgarno, 1983; Wallis, 1989) owing to preferential escape of atmospheric ^{14}N to space. Nitrogen isotopic ratios might be used to identify relatively ancient crustal rocks (R. Mancinelli, personal communication), and perhaps determine relative ages of surface samples.

As a first step in successfully measuring nitrogen isotopes optically we have demonstrated the measurement of $^{15}N/^{14}N$ to a precision of 0.1% (See Figures 1-4) using a tunable diode laser and an available gas (N_2O) with spectral lines in the 2188 cm^{-1} region. The sample and reference gas cells contained gases of identical isotopic composition so that the $^{15}N/^{14}N$ absorption ratio determined from the sample cell, when divided by the $^{15}N/^{14}N$ absorption ratio determined from the reference cell, should yield an ideal value of unity. The average measured value of this "ratio of ratios" was 0.9983 with a standard deviation (20 values) of 0.0010. This corresponds to a precision of 0.1% (1 per mil) for nitrogen isotopes, a value sufficiently precise to provide important isotopic data of interest to exobiologists. The precision presently attainable in gases

$^{15}N/^{14}N$ PRECISION ESTIMATE

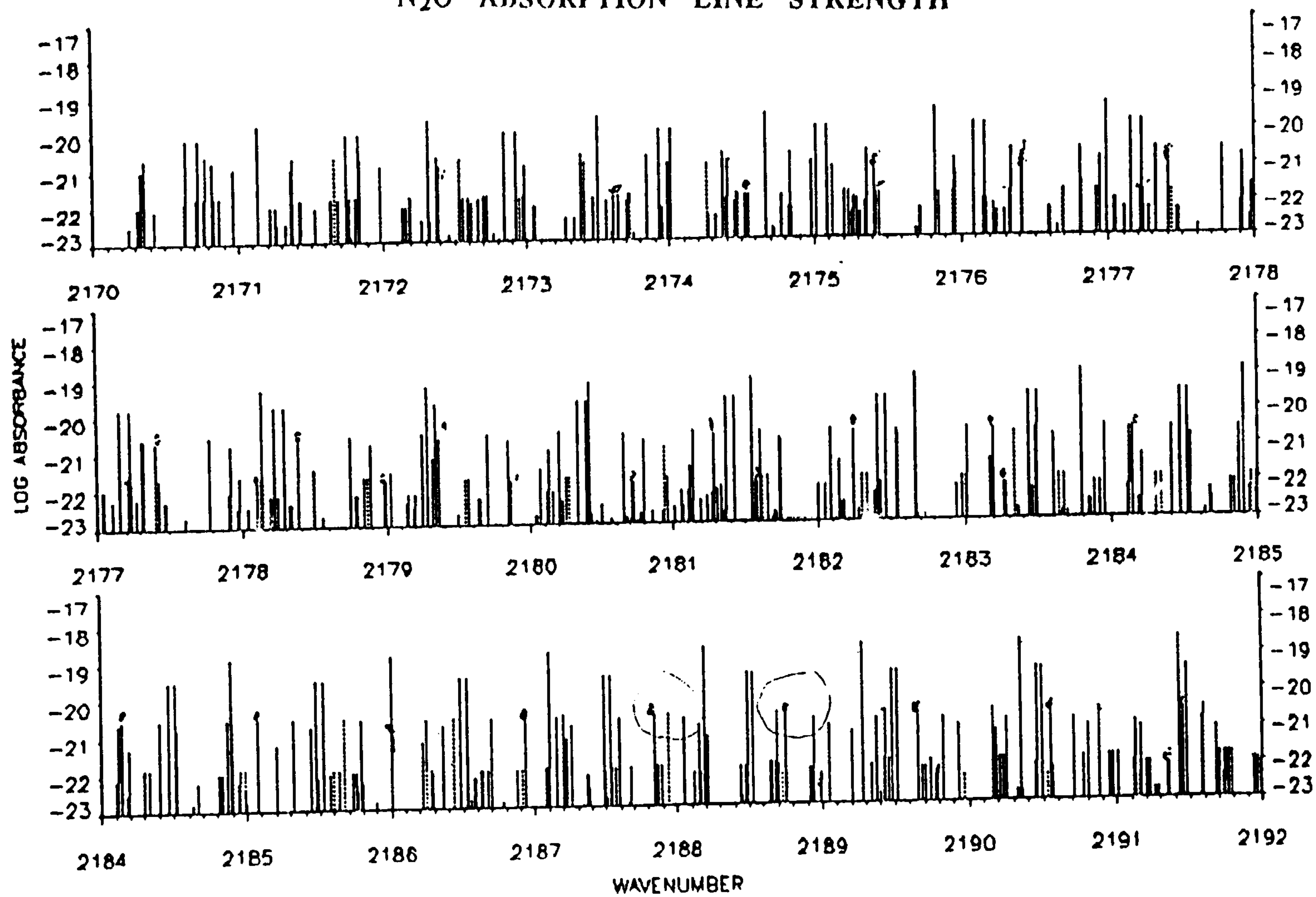
(SAMPLE AND REFERENCE GASES ARE IDENTICAL)

$$\frac{^{15}N/^{14}N \text{ sample}}{^{15}N/^{14}N \text{ reference}}$$

0.9988837	0.9998360
0.9982647	0.9988428
0.9982681	0.9991181
0.9986868	0.9984282
0.9962118	1.0000200
0.9984860	0.9979650
0.9967564	0.9992672
0.9975670	0.9973053
0.9971428	0.9975013
0.9983386	0.9993129

Average = 0.9983 **std dev = 0.0017 = 1 del unit**

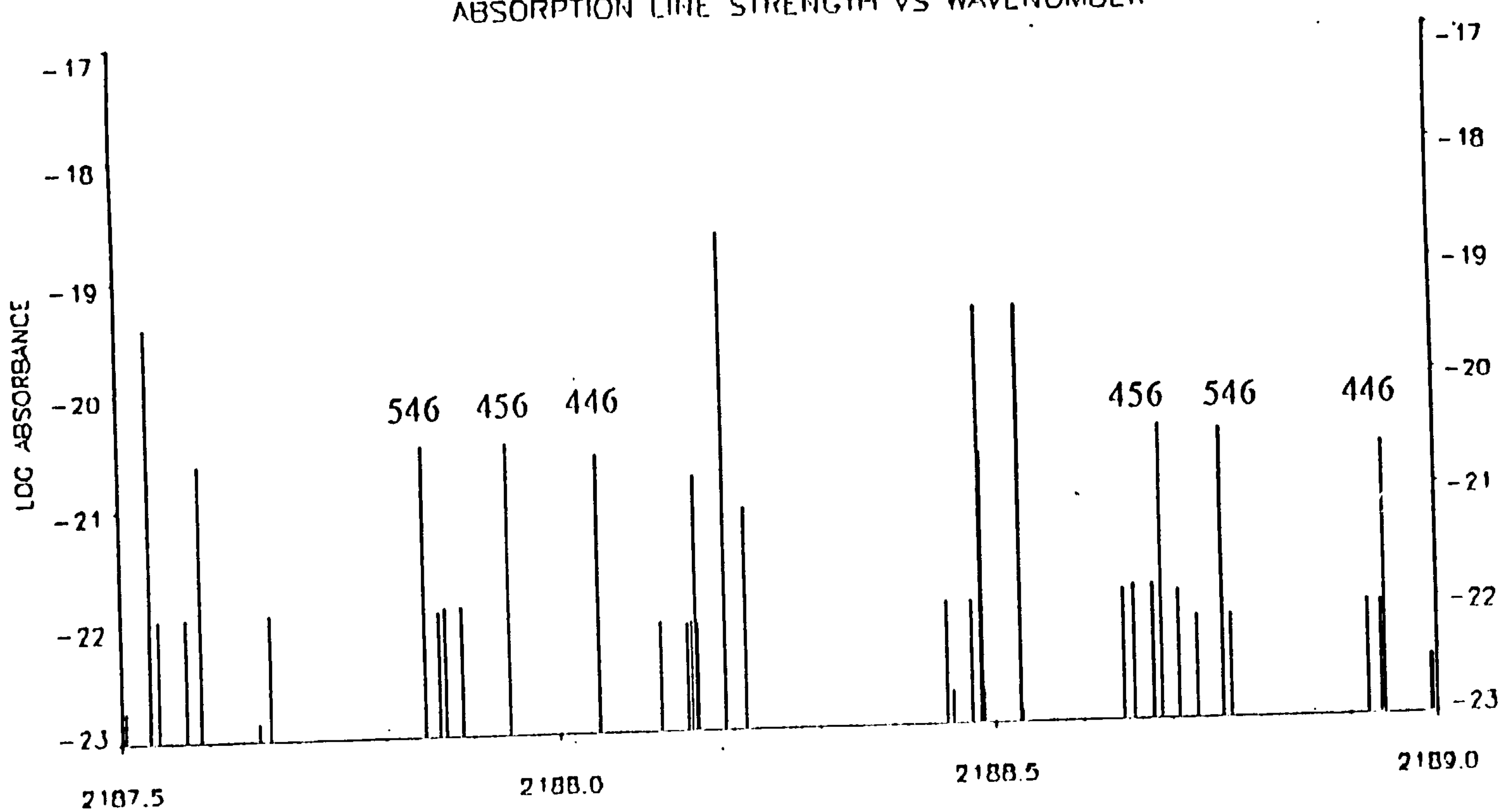
N_2O ABSORPTION LINE STRENGTH



FEASIBILITY OF MEASURING NITROGEN ISOTOPIC RATIOS USING DIODE LASER SPECTROSCOPY

- N_2O SPECTRAL ABSORPTION LINES IN 4.5 μ (2188 CM^{-1}) REGION FOR $^{15}N/^{14}N$ MEASUREMENTS

ABSORPTION LINE STRENGTH VS WAVENUMBER

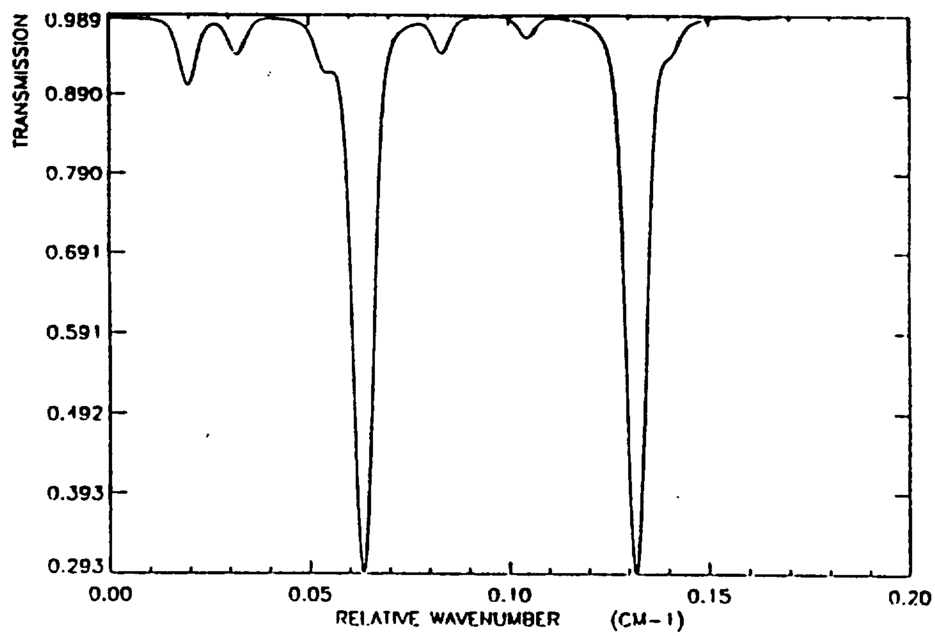


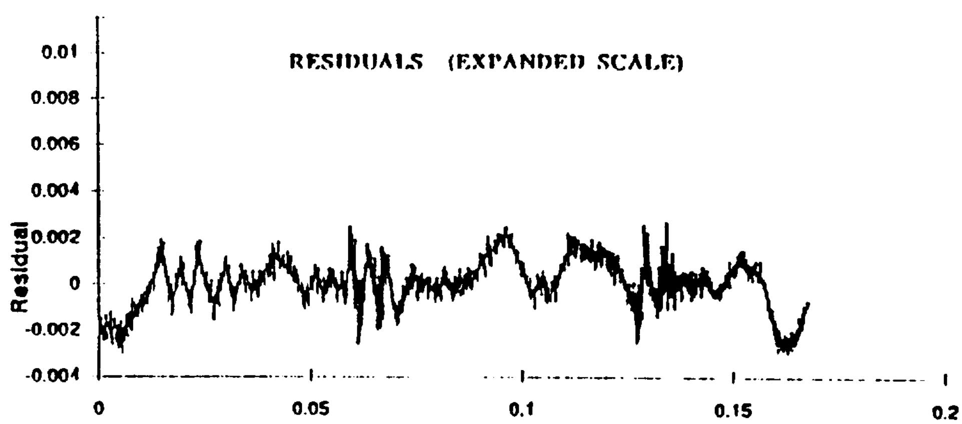
546: ^{15}N-^{14}N-^{16}O

456: ^{14}N-^{15}N-^{16}O

N_2O TRANSMISSION

DATA AND MODEL FIT





is sufficient to permit the instrument to be used in the measurement of isotopic ratios of interest to exobiologists as well as geologists and planetary scientists.

An important part of making isotopic ratio measurements in solid samples using diode lasers is the conversion of the elements of interest to molecules that have absorption spectra in the mid-ir spectral range accessible by tunable diode lasers.

We have investigated and formulated the necessary sample preparation procedures to extract nitrogen, an element of exobiological importance, from model soil compounds and to convert it to NO, a molecule with appropriate optical absorption characteristics for reliable laser spectrometer isotopic ratio measurements of $^{15}N/^{14}N$. We have considered nitrates, such as potassium and sodium nitrate, as models for the oxidized nitrogen component of the Martian regolith, and we have formulated a simple heating protocol for extracting all nitrogen isotopes in the form of NO.

The use of ion exchange columns initially proposed were determined to be too cumbersome for future use on Mars. We therefore revised our research plan and developed a protocol based on the work of Hoshino and coworkers (1981) who studied the temperature dependence of thermal decomposition products of $NaNO_3$. The chemical reactions involved are shown below:

$4NaNO_3 \text{ ----> } 4NaNO_2 + 2O_2$ (1) Reaction I

$4NaNO_2 \text{ ----> } 2Na_2O_2 + 4NO$ (2) Reaction II

$Na_2O_2 \text{ ----> } Na_2O + O$ (3) Reaction III

$Na_2O_2 + O \text{ ----> } Na_2O + O_2$ (4) Reaction III

In terms of the final products: $4NaNO_3 \text{ ----> } 2Na_2O + 2O_2 + O_2 + 4NO$. The initial process starts at temperatures just above 500 °C; the second process starts at temperatures below 680 °C and produces

NO. Hoshino and coworkers never observed N_2 production below 680^o C.

The protocol we have formulated includes thermal decomposition of $NaNO_3$ to convert all ^{15}N and ^{14}N to NO, and subsequently analyze the NO to determine the isotopic ratio of the parent analog soil, $NaNO_3$. To avoid formation of N_2 and the isotopic fractionation that occurs with such chemical reactions, thermal decomposition is done at temperatures below 680 °C. Since NO in the presence of O_2 can form NO_2 and in the process fractionate the isotopes, it is important to eliminate NO_2 production. This is done by reducing the amount of O_2 in contact with NO by initially heating the nitrate to a temperature just above 500 °C so that reaction I occurs, producing O_2 which is pumped away. In this way the total O_2 produced together with NO (reaction II) is decreased by 67%.

For the pressures and temperature involved we have calculated a characteristic time of greater than 10 hours, therefore the gas can be transferred to the sample cell of the SILS and data acquired before the amount of N going into NO_2 becomes appreciable. The accuracy of measured $^{15}N/^{14}N$ values will be studied and will depend on the amounts of nitrogen-containing compounds other than NO which are formed, and the extent of isotopic fractionation associated with the reactions involved in the formation of those compounds.

We have identified several pairs of isotopic spectral lines suitable for $^{15}N/^{14}N$ analysis of NO gas, for example the ^{14}NO and ^{15}NO spectral lines at 1872.6 cm^{-1}. There are also suitable lines of NO_2 in the 1620 cm^{-1} region that could be used if the measurement of NO_2 is found to be necessary.

This work will lead to a better understanding of the requirements necessary to successfully and accurately analyze planetary samples *in situ* on such NASA projects as the Mars Surveyor, Mars Network, Mars Micro-Rover, and Mars Rover and Sample Return.